

Allyl Ethers of Carbohydrates. II. Preparation and Polymerization of Polyallyl Ethers

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In a previous paper² the preparation of tetraallyl α -methyl glucoside was described. When this compound was polymerized, a colorless, transparent thermosetting resin was obtained. In view of the possible importance of resins of this type, an investigation of other polyhydroxy compounds was made. This paper deals with the preparation and polymerization of allyl ethers of sucrose, D-mannitol, D-sorbitol, inositol, pentaerythritol, glycerol, ethylene glycol, 1,3-butylene glycol and dipropylene glycol. Preliminary results of a study of the mechanism of oxidation and polymerization are reported, and a working hypothesis is suggested. Preparations of allylated glycerol,^{3,4} mannitol⁴ and sucrose^{4,5} have been described previously, but no physical constants have been recorded.

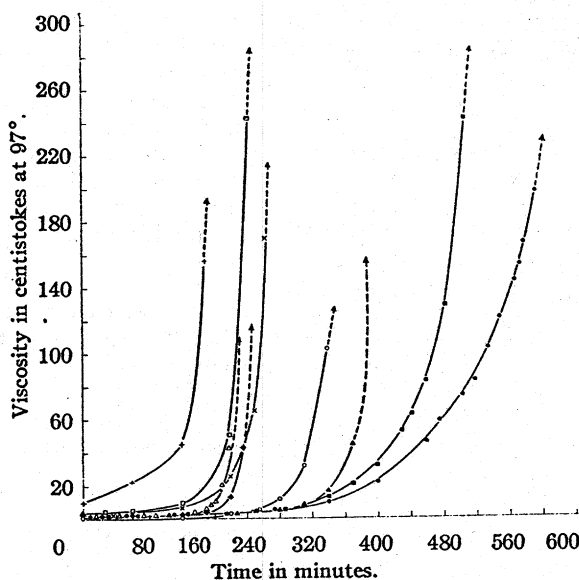


Fig. 1.—Polymerization of polyallyl ethers:

Compound	Symbol	Gelation time, min.
Triallyl glycerol	+	207
Hexaallyl mannitol	□	220
Hexaallyl sorbitol	×	240
Heptaallyl sucrose	+	207
Hexaallyl inositol	▲	350
Tetraallyl pentaerythritol	△	188
Diallyl ethylene glycol	○	315
Diallyl 1,3-butylene glycol	■	550
Diallyl dipropylene glycol	●	765

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Nichols and Yanovsky, *THIS JOURNAL*, 66, 1625 (1944).

(3) Preparation of triallyl-glycerine by Berthelot and Luca is mentioned in *Ann.*, 100, 361 (1856).

(4) Karl Frey, Dissertation, Eidgenoss. Techn. Hochschule, Zürich, 1926.

(5) Tomecko and Adams, *THIS JOURNAL*, 46, 2698 (1923).

The methods employed were essentially the same as those described in the previous paper.² Practically complete substitution was attained in most of the compounds. In general, the same type of polymerization occurred in all the compounds studied, but the rate of polymerization varied considerably, as shown in Fig. 1. It should be noted that the arrows on the curves of the graph do not represent the gelation points but merely indicate the trends of the curves. Compounds containing the greater number of allyl groups seemed to polymerize more readily, yet no clear relationship between gel points and the number of allyl groups is evident. By comparing diallyl ethylene glycol, diallyl 1,3-butylene glycol, and diallyl dipropylene glycol, the effect of structure on the time required for gelation is apparent.

During the passage of oxygen through the liquids at elevated temperatures, there was a gradual increase in viscosity followed by a rapid increase near the point of gelation. After the gelation point was reached, further heating in the presence of oxygen converted the materials containing two or more allyl groups per unit of monomer to hard brittle resins.

The solubility of the compounds in acetone and other solvents decreased as the polymerization proceeded and the viscosity increased. But even at the gelation point (viscosity, infinity), the compounds were slightly soluble. As the heating in the presence of oxygen was continued beyond the gelation point, the compound became only partly soluble and eventually was transformed into an infusible and insoluble resin.

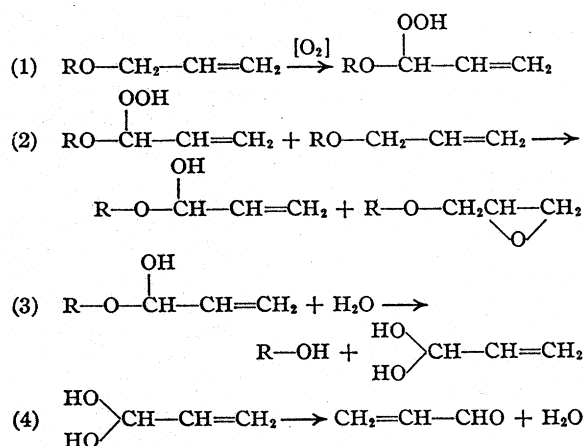
The following experiments are typical: (1) Tetraallyl pentaerythritol was gelled in the usual manner, and part of the gel was extracted with acetone in a Soxhlet extractor for forty-eight hours. It was completely transferred from the thimble to the flask containing acetone, where it gradually separated in a flaky form. (2) The remaining part of the gel was heated further in the presence of oxygen. The resulting hard brittle resin was broken into small pieces and placed in the Soxhlet thimble. Extraction with acetone for forty-eight hours removed approximately 40%. (3) A thin layer of the partly polymerized tetraallyl pentaerythritol was heated overnight at 100° in the presence of oxygen. It became almost completely insoluble in acetone.

The necessity of a supply of oxygen throughout the polymerization was indicated by several experiments in which polymerization was carried to a certain point and heating was continued in the absence of oxygen. In each case the poly-

merization proceeded normally for a short time, and then appeared to go no further. For example, it is possible to allow the polymerization to proceed nearly to the gelation point and then cause the material to gel by further heating, but heat alone will not convert the gel to the hard brittle resin, even after twenty-four hours at 100–120°.

As pointed out in the previous paper,² the formation of insoluble, infusible resins and the character of the curves in Fig. 1 suggest the formation of a three-dimensional network during the polymerization of the polyallyl ethers.

As in the polymerization of tetraallyl α -methyl glucoside, formation of peroxides was observed during polymerization of all compounds studied here. Also, a strong odor of acrolein accompanied the oxidation and polymerization of all the allyl ethers. In the study of allyl mannitol, acrolein was collected during the oxidation and identified by means of its 2,4-dinitrophenylhydrazine. If we accept the theory of Criegee, Pilz and Flygare⁶ and of Farmer and Sundralingam⁷ on the autooxidation of olefinic compounds, there is a rather simple explanation for the positive peroxide test and the formation of acrolein. The following equations would represent the course of the reaction



The first step shows formation of the hydroperoxide at the α -methylenic carbon, which in this case should be especially reactive, since it is both adjacent to an ether oxygen and in α -position to a double bond. The second step shows decomposition of the peroxide according to the scheme suggested by Farmer and Sundralingam in which the hydroperoxide oxidizes a double bond with the formation of an epoxy group. These two equations represent the application of Farmer's ideas to our compounds. The hydroxy compound formed as a result of step two is a hemiacetal, which would be readily hydrolyzed if a trace of water were present. It is evident from equations 3 and 4 that a trace of water is all that

is necessary for complete hydrolysis of any amount of hemiacetal formed, and according to Farmer's theory and our own observations water is formed during oxidations of this type.

It would be more difficult to understand how the formation of acrolein could take place should the initial peroxide have the cyclic structure $\begin{array}{c} \text{C} \quad \text{C} \\ \diagdown \diagup \\ \text{O} \quad \text{O} \end{array}$, as suggested by Engler.⁸

The formation of epoxy groups in the above-suggested scheme of oxidation and the well-known ease with which epoxy compounds polymerize led us to suspect that this group plays an important role in the polymerization and cross-linkage of allyl ethers.

The effects of various agents on the polymerization of allyl ethers in the presence of oxygen may be summarized as follows: (1) Metal salts of organic compounds, such as cobalt or manganese naphthenate or linoleate, are strong accelerators of the oxidation and polymerization process. (2) Strong acids, such as sulfuric or perchloric acid, cause extensive discoloration and decomposition at 100°, even when present in traces. Monochloroacetic acid (0.1% by weight) has no effect on the rate of polymerization, as determined viscometrically. (3) Alkalies, such as aqueous sodium hydroxide or benzyltrimethylammonium hydroxide, completely inhibit polymerization, as determined viscometrically.

The inhibition of the polymerization owing to the aqueous alkali can be explained on the basis of the hydroperoxide theory, since hydroperoxides are readily hydrolyzed by alkalies.

Experimental

Method of Preparation of Allyl Ethers

Step I. Partial Allylation of Polyhydric Alcohols.—One equivalent of the polyhydric alcohol was suspended in two equivalents plus a 10% excess of 50% aqueous sodium hydroxide in a 3-neck flask equipped with condenser, dropping funnel and stirrer. Two equivalents of allyl bromide were added dropwise to the well-stirred reaction mixture over a period of four to five hours while the temperature was maintained at 70–75°. The reaction was allowed to proceed for an additional hour, whereupon the product was extracted with ether, washed free of alkali, and distilled. The higher-boiling allyl ethers, such as those from sucrose, sorbitol, and inositol, were steam-distilled before final distillation *in vacuo*.

Step II. Complete Allylation of Polyhydric Alcohols.—The partly allylated ether was treated with an amount of sodium in slight excess of that required to react with the remaining hydroxyl groups. The sodium alcoholate thus formed was treated with an equivalent amount of allyl bromide. With lower-boiling allyl ethers, such as those from 1,3-butylene glycol and ethylene glycol, it was convenient to eliminate the second treatment with allyl bromide and distil the products from the excess sodium at temperatures lower than 100°.

Isolation of Acrolein as a By-product of the Oxidation.—Fifty grams of allyl mannitol (4.5 allyl groups) was placed in a flask equipped with a side-arm inlet tube, and a Friederichs condenser, which in turn was connected with a trap cooled with solid carbon dioxide in acetone. Oxygen was bubbled slowly through the polyallyl compound

(6) Criegee, Pilz and Flygare, *Ber.*, **72**, 1799 (1939).

(7) Farmer and Sundralingam, *J. Chem. Soc.*, 121–139 (1942).

(8) Engler, *Ber.*, **30**, 1669 (1897); **31**, 3046 (1898); **33**, 1090 (1900).

at 97° until the material gelled. The material collected in the trap weighed approximately 0.6 g. and had the pungent odor characteristic of acrolein. A strong aldehyde test was obtained with Schiff reagent. The 2,4-dinitrophenylhydrazone was prepared by the method of Brady and Elsmie.⁹ When crystallized twice from a mixture of alcohol and acetone the product melted at 164–165°. When it was mixed with pure acrolein 2,4-dinitrophenylhydrazone there was no depression in the melting point.

Determination of Unsaturation.—The percentage of allyl was determined by the Wijs method. The solvent used for the sample was glacial acetic acid. The time allowed for the sample to stand in the dark was established at four hours. As a rule, results were 0.5 to 1% lower than the theoretical values.

Calculation of Extent of Substitution.—The average number of allyl groups (n) per molecule of the compound can be calculated by determining the percentage of allyl (A) of the given compound or the percentage of free hydroxyl (H) according to the equations:

$$(1) \quad n = AM / (4107 - 40.06A)$$

$$(2) \quad n = (1700G - HM) / (1700 + 40.06H)$$

where M is the molecular weight of the polyhydric alcohol and G is the number of hydroxyl groups in the original compound. Inasmuch as the values obtained by the two methods in a number of experiments showed fair agreement, and in view of the fact that these unsaturated compounds are susceptible to oxidation, with consequent changes in the unsaturation and hydroxyl values, only the allyl content, the more direct of the two values, was determined in most cases.

Preparation and Properties of Various Allyl Ethers

Allyl D-Mannitol.—500 grams of mannitol (m. p. 165–166° uncor.) was treated with allyl bromide and sodium hydroxide as described under Step I. A main fraction of 754 g. resulted from distillation through a 12-inch Vigreux column in the range 150–160° at 0.5 mm. This material contained 4.7% free hydroxyl and 52.8% allyl. Substituting these values in equations (1) and (2) gives 4.9 and 4.6, respectively, for the average number of allyl groups per mannitol molecule. Based on a product containing 4.75 allyl groups, the yield was 74% of the theoretical.

Further allylation of the above product by Step II gave a 79% yield of hexaallyl mannitol boiling at 170–172° at 1 mm., n_D^{20} 1.4710; d_4^{20} 0.9860; viscosity at 25°, 14.52 centipoises; molecular refraction, 119.70 (calcd. 120.09); $[\alpha]_D^{25} + 14.0^\circ$; allyl, 57.5% (calcd. for $C_{24}H_{38}O_6$, 58.3%).

Allyl D-Sorbitol.—By Step I, 250 g. of sorbitol gave 373 g. of allyl sorbitol boiling at 163–167° at 1 mm. This fraction contained approximately 4.8 allyl groups per sorbitol molecule, as calculated from a free hydroxyl determination, and based on this figure the yield was 73% of theoretical.

Further allylation by Step II yielded 76% of the amount of hexaallyl sorbitol required by theory. The boiling point of this compound was 163–165° at 1 mm., n_D^{20} 1.4704; d_4^{20} 0.9837; viscosity at 25°, 12.87 centipoises; molecular refraction, 119.93 (calcd., 120.09); $[\alpha]_D^{25} + 6.56^\circ$; allyl, 57.4% (calcd. 58.3%).

Allyl Glycerol.—100 grams of glycerol allylated by Step I gave 96.4 g. of allyl glycerol boiling in the range 75–83° at 1 mm. and containing 1.1% free hydroxyl. On the basis of 2.9 allyl groups per glycerol molecule, the yield was 43% of that required theoretically. It is important to note that the yields of low-molecular weight polyallyl ethers were low, but that the degree of substitution in the first step was higher than in the case of higher-molecular weight compounds. This may be accounted for by the fact that the incompletely substituted allyl ethers of low molecular weight are more water-soluble.

(9) Brady and Elsmie, *Analyst*, **51**, 77 (1926); Allen, *This Journal*, **52**, 2955 (1930).

(10) All specific rotations were measured in 8% solutions in alcohol.

Further allylation by Step II gave an 82% yield of triallyl glycerol boiling at 82–83° at 1 mm., n_D^{20} 1.4510; d_4^{20} 0.9362; viscosity at 25°, 2.016 centipoises; molecular refraction, 61.05 (calcd., 61.15); allyl, 57.1% (calcd. for $C_{12}H_{20}O_3$, 58.0%).

Allyl Ethylene Glycol.—620 grams of ethylene glycol was treated according to Step I, and 546 g. of allyl ethylene glycol was distilled between 162 and 169°. This fraction contained 55.9% allyl, which corresponds to an average of 1.9 allyl groups per ethylene glycol molecule. The free hydroxyl was 0.87%, which also corresponds to 1.9 allyl groups. Based on 1.9 allyl groups per ethylene glycol molecule, the yield represents 40% of the theoretical.

A portion of this fraction was completely allylated by Step II and the remainder, by simply heating in the presence of sodium for two to three hours at 105–110° and distilling under diminished pressure. The latter is the more convenient method; it yields equally good results; and it is applicable to all ethers distilling below 100° under diminished pressure.

Diallyl ethylene glycol was obtained in a yield of 80%. It boiled at 35–37° under a pressure of 1 mm., n_D^{20} 1.4340; d_4^{20} 0.8940; viscosity at 25°, 0.970 centipoises; molecular refraction, 41.42 (calcd. 41.50); allyl, 57.0% (calcd. for $C_8H_{14}O_2$, 57.8%).

Allyl 1,3-Butylene Glycol.—100 grams of 1,3-butylene glycol yielded by Step I 85.5 g. of allyl 1,3-butylene glycol distilling between 44 and 50° at 1 mm. This fraction contained 42.6% allyl and 4.0% free hydroxyl, both corresponding to 1.6 allyl groups per butylene glycol molecule. On the basis of 1.6 allyl groups added, the yield represents 50% of the theoretical.

Diallyl 1,3-butylene glycol was obtained in a 60% yield by heating at 105–110° in the presence of sodium and distilling under diminished pressure. The fraction boiling between 48–50° at 1 mm. was collected: n_D^{20} 1.4330; d_4^{20} 0.8726; viscosity at 25°, 1.098 centipoises; molecular refraction, 50.70 (calcd., 50.74); allyl, 47.1% (calcd. for $C_{10}H_{18}O_2$, 48.3%).

Allyl Dipropylene Glycol.—When 100 g. of dipropylene glycol, $(CH_3CHOHCH_2)_2O$, was treated by Step I, 96 g. of practically pure diallyl dipropylene glycol (60% yield) distilled at 72–75° under a pressure of 1 mm. This material contained 0.5% free hydroxyl and had an allyl content of 37.6%. Redistillation of the product gave pure diallyl dipropylene glycol boiling at 75–77° at 1 mm.; n_D^{20} 1.4380; d_4^{20} 0.9093; viscosity at 25°, 1.717 centipoises; molecular refraction, 61.86 (calcd., 61.62); allyl, 38.3% (calcd. for $C_{12}H_{22}O_3$, 38.3%).

Allyl Pentaerythritol.—By Step I, 100 g. of pentaerythritol gave 113.2 g. of allyl pentaerythritol boiling in the range of 114–122° at 1 mm. This fraction contained 4.2% free hydroxyl and 50.6% allyl, corresponding to 3.3 and 3.2 allyl groups per pentaerythritol molecule, respectively. On the basis of 3.2 allyl groups, the yield represents 58% of the theoretical.

Further allylation by Step II gave an 80% yield of tetraallyl pentaerythritol, which boiled at 124–125° under a pressure of 1 mm., n_D^{20} 1.4595; d_4^{20} 0.9497; viscosity at 25°, 4.025 centipoises; molecular refraction, 85.38 (calcd., 85.41); allyl, 54.4% (calcd. for $C_{17}H_{28}O_4$, 55.4%).

Allyl Inositol.—100 grams of inositol treated by Step I gave 110.6 g. of allyl inositol, which boiled in the range 157–176° at 1 mm. This material contained 6.9% free hydroxyl and 51.5% allyl, corresponding to 4.5 allyl groups per inositol unit for each analysis. On the basis of 4.5 allyl groups, the yield was 55% of the theoretical.

Further allylation by Step II gave a 77% yield of hexaallyl inositol boiling at 169–170° at 1 mm., n_D^{20} 1.4788; d_4^{20} 1.0115; viscosity at 25°, 22.52 centipoises; molecular refraction, 117.85 (calcd., 117.89); allyl, 57.4% (calcd. for $C_{24}H_{38}O_6$, 58.6%).

Allyl Sucrose.—Allyl sucrose was prepared by Step I in a 68% yield based on 7 allyl groups per sucrose molecule. The product, which was extremely high boiling, was finally distilled in a molecular still at a pressure of 5 microns and a bath temperature of 190–192°. Analysis of the dis-

tillate showed that the product corresponded roughly to heptaallyl sucrose: n_D^{20} 1.4912; d_4^{20} 1.1071; viscosity at 25°, 792.5 centipoises; $[\alpha]_D^{25}$ +50.5°; molecular refraction, 163.01 (calcd. for heptaallyl sucrose, 164.79); allyl, 44.3% (calcd. for $C_{31}H_{50}O_{11}$, 46.2%).

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Summary

1. Allyl ethers of D-mannitol, D-sorbitol, glycerol, ethylene glycol, 1,3-butylene glycol, dipropylene glycol, pentaerythritol, inositol and sucrose have been prepared and their polymerization has been studied.

2. A possible mechanism of oxidation of allyl ethers of polyhydric alcohols is discussed.